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Electro-Deposition of Iron from a Chloride Bath

Charles W. Noon

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FROM A CHLORIDE BATH

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A Thesis

Submitted to the Department of Metallurgy

in Partial Fulfillment of

the Requirements for the Degree of

Bachelor of Science in Metallurgical Engineering

Montana School of Mines

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ABSTRACT

Iron was electro-deposited from a ferrous chloride bath. Studies were made of deposits formed when current density was varied, and finally when both current density and temperature were changed. An attempt was made to lay the ground work for a long range study of the chloride bath, and to determine the most simple conditions possible for obtaining a smooth, even, and thick deposit; particularly, one free from cracks and pits. Other deposits were made from the sulfate bath, such that a comparison of the quality of the two could be made. A review of the history of electrolyte iron, its uses and properties, and the latest information on research in the chloride bath were also included. The laboratory equipment, and the electrolyte employed in this work were described.

INTRODUCTION

Although electrolytic iron has been known for almost one hundred years, it has always remained one of minor importance in the plating world. Many factors influence this obscurity, but the two prominent ones are sufficient to explain it. The first lies in the fact that electro-deposition, as a means of obtaining iron as such, has been continually pushed into the impractical by other well established and cheaper methods. The other lies in the fact that electrolytic iron, with properties which make it desirable for specific uses, has been ever replaced by other metals. These metals can be produced at a low cost, are abundant, and have special properties that make them better than electrolytic iron. Though its history is one primarily of laboratory interest, with a few brief flurries of commercial interest, and though the above conditions have prevented its becoming of importance up to the present time, research on electrolytic iron

is being continually carried foreward.

HISTORY

The first recorded work on electrolytic iron was produced by Botteger, a German chemist, in 1846, in which he showed the results of various laboratory experiments on the subject. A lull followed in which interest centered mainly in the laboratory, with the gathering of information and examining results for possible commercial value. In 1868, Klien, Jacobi and Maximowitsch found it useful for plating copper engravings that were used for printing Russian bank notes. It was employed in this manner for many years since it provided a hard and durable coating, with the added advantage that printing could go on until the copper began to show through, whereupon the engraving could be replated. Finally, however, nickle replaced it for this use. Except for this particular item, electrolytic iron remained in obscurity until 1904. At this time Burgess and Hambuchen, in America, produced a deposit which created the first flurry of commercial interest. Their method, modified by Watts, was the basis for the construction of the electrolytic refining plant of the Western Electric Company at Hawthorne, Illinois. A ferrous and ammonium sulfate solution was employed with a current density of 6-10 amps/sq. foot, an emf. of less than one volt, a temperature of 30°C, and anodes of wrought iron. Ammonium oxalate was used as an addition agent. The low production of 1000 pounds of iron per week, together with the high cost, soon forced the plant out of existence. The same year found an English chemist, Cowper-Coles, developing a method employing a 20% solution of Sulfo-Cresylic acid charged with suspended iron oxide, a c.d. of 100 amps/sq. ft., a temperature of 70°C, and a rotating cathode. No production of commercial importance arose from this development, although it was later claimed that the plant at Grenoble,

France, was based on his idea.

In 1908, the Fischer-Langbien Pfanhausen, a German concern, developed an electrolyte of ferrous and calcium chlorides, from which a good, pure deposit was obtained. The current density ranged up to 200 amps/sq. foot, and the temperature was 90°C. Hughes, of England, studied this and took out British patents on the same.

From a commercial standpoint, 1910 seemed to be the year that the high point in electrolytic iron was reached. Boucher and Bouchayer, French chemists, developed a solution which seemed promising, and later Bouchayer formed the company, Societé "Le Fer", and constructed a plant, which was quite complete. The process consisted of the refining of cast iron to form a finished tube. The electrolyte was ferrous chloride, made up of scrap iron and HCL, with a specific gravity of 1.5; of which, none was discarded. It was kept at 70-75°C, but temperature control was difficult. The electrolyte was circulated rapidly, and before returning to the cell was passed over iron filings to insure neutrality. The iron filings also acted as a filter. The company claimed that the noxious effect of the H_2 liberated at the cathode was overcome by the oxychloride of iron which the solution carried. At first the oxychloride was made by areating the solution in the scrap tanks, but was later accomplished by a slight electrolytic oxidation of the solution using an insoluble anode. The plant employed two rows of cells, and each row was a separate circuit. The anodes were two L-shaped castings, and during the process were about 80% dissolved. The cathode was a rotating mandrel, 85-160 mm. in diameter and 4 meters long, mounted on wooden bearings. The mandrels were rotated at various speeds depending on the diameter, the 160 mm. diameter cathode being run at 180-220 RPM. If the bearings were not worn the iron deposited smoothly as a thin tube on the mandrel; if rotation was not even the deposit was irregular and of uneven thickness. The

thinnest tube was 2 mm. thick, and the thickest was 5 mm., and it was at this point that the company claimed the efficiency of their system. In the formation of tubing by drawing, dies are needed for each reduction in size, and the resulting tube had to be treated to eliminate undesirable properties produced by the drawing process. The electrolytic formation, on the other hand, could be controlled in the one operation, obtaining the desired thickness, and a finished tube. This, the company claimed, resulted in large savings, particularly in labor.

The power supplied was 1000 amps and 100-130 volts, giving a current density of 70 amps/sq. ft. and a voltage per cell of 3-4 volts. After deposition, the mandrel was placed in a slowly revolving lathe which carried a traveling, double gas jet. This removed enough hydrogen so that the tube could be removed without cracking. The tube was removed by compressing the deposit by means of three traveling rolls which were hydraulically forced against the deposit. The pressure was sufficient to expand the iron circumferentially so that the tube came entirely loose from the mandrel. It was then removed and given a full anneal in an open flame, continuous furnace.

Before the mandrels could be used again they were scoured and polished, and placed as the cathode in a bath of lead perchlorate. Insoluble anodes were used, and a light coating of lead was plated on these mandrels. The lead acted as a rust preventative, so that stripping of the tube would be facilitated by the presence of this soft, easily fusible layer between the steel mandrel and the iron deposit. Total production was about 2 tons per day. The product was used in special radiator work requiring tubes of high ductility. Their advantage lay in that they could easily be drawn into complicated shapes, and easily welded. The plant operated some fifteen or twenty years before economic reasons forced it to close.

In 1911, Fischer developed a chloride bath, but no information on it

could be found for this writing. The same year, Remagé received patents on a process for the deposition of iron from an iron ore. Briefly, the ore was leached in H_2SO_4 and reduced to the ferrous state by SO_2. However the process was too complicated and required too close a control; no commercial value came from it.

The year 1913 saw a great deal of activity with regard to all metals as World War I approached. In electrolytic iron, the previous methods and solutions were restudied, the only new one being a patent taken out by Reed in which he obtained the iron with H_2SO_4 as a by-product. World War I saw the Germans, employing the method of the Fischer-Langbien Pfanhausen (1908) as a substitute for copper in shell bands and casings and for needed bulk iron. It also saw the British and Americans using the electrolytic iron as a means of building up worn machine parts. The method was good only for thin coatings; if thicker ones were desired they were made up of successive thin layers, the surface of each being ground and carefully treated to receive the next. Both chloride and sulfate baths were used, giving a good adherent deposit, which was the object desired. Just how good these were is evidenced by the fact that the part could be bent in any shape, hammered, or twisted, and the bond would not separate.

In 1921, the Milford Electrolytic Iron Company was formed to produce a deposit, electrolytically, from the ore. This method was based on the Eustis-Perin process, but revised and improved at laboratories in Cambridge, Mass. Briefly, finely ground oxide ores were leached in dilute HCl and reduced to the ferrous state by SO_2. This leach was then electrolyzed, to obtain the iron deposit. The free acid formed was to be used as a leach for more ore. The plant was quite large and complete, and some success was obtained. However, like nearly all other methods, it proved short-lived. A plant was erected in 1925 at Niagara Falls, N. Y., based on the Bouchayer plan. Even

with the abundance of cheap electric power available here, it too had a short life.

In 1930, a process was reported in which intaglio plates for printing government currency and bonds could be made. This consisted of backing a nickle face with a heavy deposit of electrolytic iron. A hot chloride bath with a C.D. of 60 a/sq. ft. was recommended. The method proved valuable, and is used today by the Bureau of Engraving at Washington, D. C.

Work done at Battelle Memorial Institute in 1939 showed that the embrittlement of the deposited iron is produced physically by hydrogen that occludes under steel rupturing pressures in the ultra-microscopic rift system, commonly identified as slip or cleavage plane structure. The advent of World War II, as in the first one, probably created a renewed interest, but it is too soon to receive the findings of this period. The latest application in the electroforming of iron has been worked out by the United States Rubber Company. The process has been applied to the manufacture of molds for tires, plastics, die castings, etc. No data on the plating solution is available to date.

Biblio. 1-14-15

USES OF ELECTROLYTIC IRON

As stated before, electrolytic iron has few and limited uses today. However, a few possible ways in which this iron could be employed would seem worthwhile. No mention is made of the practicability of these uses.

Since it is very brittle, it can be easily broken up or powdered. That coupled with its high purity makes it ideal for melting in a crucible. The occluded hydrogen has the further advantage of helping to maintain a reducing atmosphere.

The ease of breaking and powdering plus its high rate of corrosion by acids (before annealing) makes it possible to employ the iron as a substitute for zinc in the manufacture of hydrogen by acid attack.

Its high purity makes it possible to compete with Swedish iron at approximately the same cost.

Due to its high purity, another use is for pharmaceutical purposes as a base for compounds of which iron is a constituent.

In spite of the failure of the Bouchayer plant (see page 5), it could be used for the production of sheets and tubes of great uniformity.

It is used as a basis for scientific experimental work on the various properties of iron where the purest available iron is needed.

It is used as the basis for "pure iron" alloys.

It is used in the production of electrotypes and intaglio printing plates.

Biblio. 4, 7.

PROPERTIES

From an engineering viewpoint, the mechanical properties are the most important. They vary widely, depending upon the bath composition and conditions of operation. For the metal as deposited, Kasper reports a Brinell hardness number of 127 for a deposit from a chloride bath made at 93 a/sq. ft. with a bath temperature of 102°C. Usually the metal is much harder, having a Brinell hardness number of 360. For a soft deposit similar to the one just mentioned, Kasper reports a tensil strength of 61,000 lb/sq. inch and an elongation of 18%. This agrees with the data of Thomas & Blum, who report a tensil strength of 56,000 lb/sq. inch and an elongation of 20% for a metal deposited from a chloride bath with a C.D. of 65 a/sq. ft. and a

temperature of 90°C. For harder deposits the tensile strength increases as high as 113,000 lb/sq. inch while the elongation falls as low as 0%.

Annealing affects the mechanical properties profoundly. After annealing at a temperature sufficient to cause recrystallization, i.e., about 900°C for unformed metal, the mechanical properties approach those of open hearth ingot iron, with the tensile strength approximating 40,000 lb/sq. inch and the elongation 30 to 40%. The Brinell hardness number drops to 90 or lower. An annealing temperature of 500°C is sufficient to remove most of the effects of cold working.

LATEST RESEARCH ON THE CHLORIDE CELL

As was mentioned previously in the history, research was continually carried on and is, indeed, going foreward today. Since the main aim of this thesis is the laying of ground work for future study, it seems most appropriate to record merely the latest results of research. These are as follows:

1. Relatively soft ductile iron can be deposited from a bath containing 5N $FeCl_2$ and 0.10 N HCl at a temperature of 106°C and a C.D. of 186 amp/sq. ft.

2. Under any given conditions, softer deposits are produced by increasing the acidity, by increasing the temperature, or by decreasing the current density.

3. Additions of boric acid or calcium chloride to the baths have little effect on the properties of the deposit. KCl leads to brittle deposits.

4. The harder deposits are finer grained and contain more oxygen than the softer deposits.

5. The rapid production of dense, ductile iron deposits, free from roughness or pits, requires very careful control of all factors, especially

the acidity and temperature, and the use of effective diaphragms, preferably made of blue asbestos cloth.

6. The solution should be clear green in color, i.e., nearly free from ferric salts. Ferric salts tend to reduce cathode efficiency and cause brittle deposits.

7. A high concentration of ferrous chloride is desirable, at least 4N and preferably 5N. With lower concentrations more brittle deposits are obtained.

8. The acidity (rather than the Ph) should be controlled within fairly close limits. Insufficient free acid leads to brittle deposits, while excess acidity lowers the cathode efficiency.

9. The temperature is the most important single factor, as variations of 5°C may produce a marked change in the properties. In general, under given conditions, a decrease in temperature decreases the ductility.

10. The addition of small amounts of manganese chloride to the solution is effective in producing ductile fine grained deposits. It also broadens the temperature and Ph range considerably.

11. The improved bath, which is the best to date, consists of the following:

200 to 500 g/L $FeCl_2 4H_2O$
3 to 5 gm 1L $MnCl_2 4H_2O$
1 gm 1L gardinol WA powder
Temp - 70-105°C
Ph range 1.5-2.5
C.D. - 50 amp/sq.ft

Biblio. No. 13

LABORATORY WORK

Equipment

The laboratory equipment necessary for the experimental work was quite simple, and could be easily duplicated.

Power was obtained from the standard 60 cycle, 110 volt "house distribution" line, and changed over by a B&L portable rectifier producing two amps continuously or three amps intermittently at 115 volts.

This small working amperage, and the wide range of current densities required, were the factors influencing the choice of cell sizes. The choice of electrolyte carried with it a footnote that current densities up to 186 amps per square foot were desirable, but did not explain the factors by which any certain amount was particularly desirable. Thus for low densities, a large cell could be used, but with very high densities and the amperage available, small cells were needed. All cells were of glass produced by cutting the bottoms from bottles by means of a diamond saw.

For the deposition with respect to change in temperature, the above cells were unsatisfactory because the internal stresses were too great. When rapid changes in temperature occurred, they broke. Thus, for this phase of the investigation, 250 m.l. beakers were used, and were entirely satisfactory.

The cells were of the following sizes:

1 5/8" x 2 1/4" x 1 1/2" deep
2 1/8" x 2 1/8" x 2 1/2" deep
4 1/2" x 7 1/2" x 4 1/2" deep
250 m.l. circular beaker

The electrodes were not varied throughout the investigation.

The anodes were .170" Armco iron, having a carbon content of 0.016 percent. The heavy oxide coating and considerable grease required that they be cleaned by passing over a sanding machine and careful wiping. Be-

fore using they were immersed in a dilute solution of nitric and hydrochloric acids, washed, immersed in alcohol, and dried over a flame.

The cathodes were of thin copper sheeting, and they too were sanded, given the same immersion treatment, and dried over the flame. As the investigation proceeded, it was found that the smoother they were the better was the deposit. So later, after sanding they were polished and then cleaned by immersion and dried. This polishing required considerable time, but it is believed that the increased grade of deposit made it well worth the extra time and work.

For the large cell a commercial, clamp type spacer was used. This laminated form made regulation of electrode distance a simple matter. However, for the small cells and beakers the clamps were too large so holders were constructed employing strips of wood insulated with rubber tubing and wired together. The small electrodes could then be forced into these holders, and held securely. The cathode distance was then regulated by moving each separate holder back and forth along the cell to the desired distance. This method was none too satisfactory as a uniform distance was difficult to maintain after connecting to the power supply. Any bumping or jarring disrupted the electrodes with the result that the spacing was thrown off and voltage fluctuated madly. A little ingenuity on the part of some future investigator could produce a much more desirable holder.

Amperage was read by means of an ammeter reading in milliamps, and voltage, by means of a voltmeter reading in tenths of a volt.

Agitation was accomplished by means of a variable speed, mechanical agitator employing a glass rod stirrer.

Heat was supplied by means of a bunsen burner, and the temperature controlled by a thermometer reading in degrees centigrade, and graduated in tenths of a degree.

Miscellaneous equipment consisted of insulated copper wire, a ring stand, wire screen, asbestos, clamps, and a single throw switch.

Electrolyte

It was desired, for the laboratory work, to choose the most simple and economical bath possible, and yet one from which a good deposit could be obtained. The effective blockade by the Allies, in 1918, forced the Germans to strongly investigate electrolytic methods for the production of badly needed iron. After considerable investigation they chose the solution developed by Fischer and Langbien in 1908. It is certainly a simple and economical one, and although little information is known of their production, they did produce good deposits. This was the bath chosen for this thesis.

It consisted of the following: [1]

$FeCl_2\ 4H_2O$	300 grams
$CaCl_2$	335 grams
Water	1 Liter
Temperature	90°C
C.D.	up to 186 amp/sq.ft.

Ferrous salts alone are suited to iron deposition as ferric salts reduce the cathode efficiency and produce brittleness.

No ferrous chloride was available, and it was necessary to prepare it by reducing ferric chloride to the ferrous state. This was done by passing a stream of hydrogen through a concentrated solution of $FeCl_3$, in the presence of an excess of iron filings, till such time as reduction was complete. The time required for this is approximately six hours. After complete reduction, the material was filtered through a vacuum filter, and the filtrate boiled to dryness. While taking to dryness, some oxidation took place and was evidenced by streaks of the yellow, ferric form. This at first caused some alarm as it appeared to be present in some quantity. Later examination showed that the actual amount present was negligible and did not interfere.

Due to the ready oxidation of ferrous iron to ferric iron, the ferrous solution must be constantly protected from the air. The object of the calcium chloride is to reduce evaporation and oxidation. It further increases conductivity and decreases the metallic ion concentration. It has no effect on the properties of the deposit.

These two compounds were weighed out carefully, and dissolved in a liter of distilled water. To speed up dissolution, the bottle was placed on rolls and revolved for about an hour. Finally the solution was again filtered, and was obtained as the clear green, ferrous electrolyte.

Other investigators claim that as long as the electrolyte remains clear and green, the ferric iron content is below the trouble point. Upon standing in a stoppered bottle, the electrolyte took on a yellowish color and a precipitate formed. Filtration removed all of it and was done each time it occurred. As the work progressed, it was found to be a hydroxide, and further, that it seemed to have no effect on the deposit. This may have been influenced by the low carbon content of the anodes. It is known that the carbon liberated by anode dissolution is suspended in the electrolyte for considerable time but finally settles to the bottom. Were it present in any considerable amount, it is conceivable that the hydroxide would hold it in suspension long enough to travel to the cathode where it would be redeposited with the iron.

The statement has been made that organic impurities in solution cause brittleness, and it is believed that those commonly encountered are not harmful.

Other investigators have shown that the pH of the solution must be carefully controlled. They have found that without close control the acidity of the solution changes rapidly. Due to the small cells used, it was possible to discard the solution for each run, and it was believed that no

trouble arose from pH control as the time of deposition was too short for much oxidation. The pH of the solution was 4.9 immediately after preparation, but soon settled down to 1.8. Here it remained for the rest of the examination. Evans [4] stated that high acidity wastes current through evolution of hydrogen, and further causes excessive pitting. He also claimed that lowering of the acidity increases current efficiency. Blum and Hogaboom believe a pH of 1.8 is ideal.[2]

Experiments

The aim of the laboratory work done by Mr. Irving M. Kenoffel in his thesis of May 1943 was to produce as satisfactory a deposit of Fe as was possible from the sulfate bath. The electrolyte and conditions of deposition that he used for his most satisfactory deposit were followed closely, the object being to determine the best deposit that he obtained from a sulfate bath that a comparison could be made with the best one obtained from the chloride bath. The first four tests are on the sulfate bath.

Electrolyte and conditions of deposit:

$FeSO_4$ $7H_2O$	150 grams
$(NH4)_2$ SO_4	100 grams
Ammonium oxalate	10 grams
Water	1 Liter
C.D.	19 amps/sq.ft.
Voltage	2 volts
Time	24 hours

Test No. 1 (Kenoffel's No. 12)

Cathode area	2 3/8" x 2"
Amps	.8
Voltage	.85
Cathode distance	1 5/8"
Time	1 hour

The deposit was good in color, being gray and bright, but badly cracked. It had a tendency to curl as it built up. It also contained combined hydrogen and consequently was very brittle. Kenoffel stated that 24 hours was desirable, with 48 hours the maximum before cracking occurred. In

this instance cracking occurred at 1 hour, so the test was discontinued as soon as cracking was detected.

The amperage remained constant throughout the time, but voltage fluctuated from .86 to .85, and toward the end of the hour dropped evenly to a final of .76 volts.

Test No. 2

All of the conditions of No. 1 were maintained, with identical results.

Test No. 3

Same electrolyte
Cathode area. . . . . 2" x 3"
Iron anode. . . . . 0.16% C

Polished copper cathode
Amps. 496
Voltage 63
Cathode distance. . . . . 7/8"
Time. . . . . 1 hour

The deposit was again gray and bright, and was rather smooth but patchy. It was decided to allow another hour, but no improvement was seen. Left to run over night (some 18 hours) a good thick deposit was obtained, but it was very brittle and badly cracked. The electrolyte was almost completely depleted. The amperage remained constant during the time of observation while the voltage fluctuated between .63 and .61.

Test No. 4

Due to the smooth but irregular deposit of No. 3, it was decided to maintain the same conditions but grease the cathode lightly with vasoline. The ensuing deposit was again gray, bright, and badly cracked. Believing that an important condition obtained by Mr. Kenoffel was missing, it was further decided to proceed with the chloride bath.

Test No. 5

Since the German investigators recommended a high current density for the electrolyte, the deposition was started at a relatively high one.

Iron anode. . . . . .016 carbon

Copper cathode
Cathode area. . . . . .01 sq. ft.
Cathode distance. . . . . 7/16"
Current density . . . . . 120 amps/sq. ft.
Current . . . . . 1.2 amps
Voltage . . . . . 1.6 volts
Time. . . . . 7 minutes
Temperature . . . . . 25°C

Terrific gassing took place immediately and within seven minutes bad cracks appeared, with some of the deposit dropping to the bottom of the cell. The test was stopped as it was evident that no good deposit could be obtained. An examination of the iron showed it to be rather bright and gray but very badly pitted as well as cracked. The results indicated that the current density was much too high.

Test No. 6

Electrodes. . . . . Same
Cathode area. . . . . .0144 sq. ft.
Cathode distance. . . . . 7/16"
Current density . . . . . 59 amps/sq. ft.
Current . . . . . .85 amps
Voltage . . . . . .752 volts
Time. . . . . 1 hour
Temperature . . . . . 25.1°C
pH. 1.74

After examining the deposit produced in Test No. 5 the C.D. was cut in half and the electrode distance controlled such that the voltage should also be cut down. The current remained constant throughout, but the voltage fluctuated from .752 to .700 in 15 minutes, to .655 in 30 minutes, to .65 in 45 minutes, and remained as such for the remaining time. A rapid evolution of gas appeared almost immediately but dropped off until barely noticeable after 30 minutes. The coating was quite uniform during the first 15 minutes, whereupon cracks appeared, and was badly cracked and pitted in one hour. The color was bright gray.

Wt. of cathode + deposit. . . 14.1920 grams
Wt. of cathode before deposit. 13.0984 grams
Wt. of iron deposit. . . . . 1.0936 grams

$$\frac{.85 \times 60 \times 60}{96500} \times \frac{55.85}{2} = .886$$

$$\frac{1.0936}{.886} = 123\% \text{ eff.}$$

It was believed that a weighing error caused this high C.E.

Test No. 7

Cathode area	.01 sq. ft.
Cathode distance	7/16"
Current density	45 amps/sq. ft.
Current	.45 amps
Voltage	.657 v
Time	1 hour
Temperature	26°C
pH	1.78

The plan of reduction in C.D. was again followed. The current remained constant but the voltage dropped from .657 to a final of .64 volts. The deposit was very smooth and even for about 12 minutes, whereupon cracking appeared. In one hour the deposit was badly cracked but less pitted. The iron formed was extremely brittle, and rusted quickly upon standing in air. Very little gassing occurred during the test.

Test No. 8

Same conditions as Test 7 except for a further reduction in C.D. and an increase in cathode distance.

Cathode distance	11/16"
Current density	25 amps
Current	.25 amps
Voltage	.60 v

The deposit was smooth, bright, and of a silvery lustre, but brittle. At 47 minutes, slight cracking appeared along the bottom edge and the upper left hand corner of the cathode. Only a small evolution of gas and evenly distributed over the surface occurred. Slight pitting. This was the first test to give hopeful results.

Test No. 9

The same conditions of test No. 8 were maintained, but agitation included to prevent the pitting which resulted from gas bubbles adhering to the cathode surface. However, exactly the same results were obtained as in No. 8.

Test No. 10

Cathode area	0.0312 sq. ft.
Cathode distance	3/4"
Current density	17.6 amps/sq.ft.
Current	.55 amps
Voltage	.455 v
Time	1 hour
Temperature	26.2°C
pH	1.8
Agitation	

The deposit was inferior, light gray in color, and had a silver lustre. There was no cracking, but the coating was badly pitted. A large quantity of solution was absorbed by the deposit, and a number of washings were necessary before extrusion of the electrolyte was stopped. The iron quickly rusted in air. The absorbed electrolyte noticed here may account for the high efficiency of Test No. 6. The pitting occurred even with agitation, so it was questionable whether agitation affected the deposition.

Wt. of cathode + deposit	23.2766 grams
Wt. of cathode before deposit	22.6892 grams
Wt. of iron deposit	0.5874 grams

$$\frac{.55 \times 60 \times 60}{96500} \times \frac{55.85}{2} = .573 \text{ grams (Theoretically)}$$

$$\frac{.5874 \times 100}{.573} = 102.5\% \text{ Efficiency}$$

A titration with .00462 standard dichromate solution gave a purity of 99.69% iron.

Test No. 11

Since the low C.D. of No. 10 produced no cracking, it was decided at this point to raise the current density till cracking appeared. Thus, a

range of C.D. could be determined wherein a smooth deposit could be made.

All conditions of No. 10 were maintained except:

C.D. . . . . 20.8 amps/sq. ft.
Current . . . . . .65 amps
Voltage . . . . . .66 v

Little gassing occurred during the deposition. The deposit was dull gray, badly cracked, and rusted quickly in air.

Test No. 12

All conditions of Test 10 were maintained except:

C.D. . . . . 19 amps/sq. ft.
Current . . . . . .594 amps
Voltage . . . . . .50 v

The deposit was light gray, smooth, had a silvery lustre, but rusted quickly. Thus for 1 hour's time, the optimum C.D. for smooth deposition lies between 19 and 20.8 amps/sq. ft. However, it was allowed to deposit for a half hour longer, whereupon cracking appeared.

Test No. 13

All conditions of Test No. 12 were maintained except the cathode was greased lightly with vasoline. The voltage jumped to .70 volts. The deposit was not smooth, but not cracked or badly pitted. The cathode showed through in several spots. The color was dark gray. No gassing was apparent, but a frothy condition surrounded the cathode. It was allowed to run another hour with no change in conditions from those of the first hour.

Test No. 14

The size of the cell may have affected the deposit, so with the same conditions of Test 12 the deposition was carried out in the large cell.

C.D. . . . . 19 amps/sq. ft.
Current . . . . . 0.588 amps
Voltage . . . . . 0.654 v

The deposit was unchanged from that obtained from No. 12.

Wt. of cathode + deposit. . . 55.5821 grams
Wt. of cathode before deposit 55.9138 grams
Wt. of iron deposit . . . . . 0.6683 grams

$$\frac{.59 \times 60 \times 60}{96500} \times \frac{55.85}{2} = .6416 \text{ grams (Theoretically)}$$

$$\frac{.6146}{.6883} \times 100 = 91.9\% \text{ Efficiency}$$

Test No. 15

Cathode area. . . . . 0.027 sq. ft.
Cathode distance. . . . . 3/4"
Current density . . . . . 57.5 amps/sq. ft.
Current . . . . . 1.6 amps
Voltage . . . . . 0.653 v
Time. . . . . 1 hour
Temperature . . . . . 40°C
pH. 2.0

The deposit was even, showed no cracking, but was pitted extensively at the center of the cathode. The color quickly turned to dark gray; considerable gassing on both anode and cathode took place. Much solution was combined in the deposit, requiring 5 washings to remove all.

Test No. 16

Cathode area. . . . . 0.0208 sq. ft.
Cathode distance. . . . . 3/4"
Current density . . . . . 77 amps/sq. ft.
Current . . . . . 1.6 amps
Voltage . . . . . 0.60 v
Time. . . . . 1 hour
Temperature . . . . . 60°C

The deposit was evenly distributed but rather badly pitted. No cracks were noticeable. Gassing appeared at both electrodes. The voltage dropped to final of 0.60 volts.

Test No. 17

Cathode area. . . . . 0.014 sq. ft.
Cathode distance. . . . . 3/4"
Current density . . . . . 100 amps/sq. ft.
Current . . . . . 1.39 amps
Voltage . . . . . 0.64 v
Time. . . . . 1 hour
Temperature . . . . . 80°C

The deposit was excellent, being very even and regular, with no signs of cracking or pitting. The color was light gray and had a silvery lustre. A number of washings were required to remove the combined solution.

Test No. 18

The same conditions as No. 17 were maintained, with the following changes:

C.D. . . . . 150 amps/sq. ft.
Current . . . . . 2.10 amps
Voltage . . . . . 0.755 v
Temperature . . . . . 90°C

Again the deposit was excellent, but to all appearances no better than in No. 18. The boiling point of the solution was nearly reached, and the ensuing agitation produced a rather large amount of sludge, which appeared to have come from anode dissolution. It was difficult to tell whether gassing took place or not, however, the deposits from Nos. 17 and 18 were excellent and, most certainly, the best obtained throughout the testing work.

Wt. of cathode + deposit. . . 12.1615 grams
Wt. of cathode before deposit 10.0772 grams
Wt. of iron deposit . . . . . 2.0879 grams

$$\frac{2.1 \times 60 \times 60}{96500} \times \frac{55.85}{2} = 2.19 \text{ grams (Theoretically)}$$

$$\frac{2.088}{2.19} \times 100 = 95.5\% \text{ C.E.}$$

Titration with .00462 standard dichromate solution gave a purity of 99.84 percent iron.

DISCUSSION

Upon starting the thesis, the Fischer-Langbien solution [2, 8] seemed best suited to a study of the chloride bath. It was developed by two respected electroplaters, had been commercially used, was the most simple and economic, and had the best description and data available. The information on con-

ditions and results obtained from the same source[2] were too general, and too much was lost determining why any set of conditions was used. The solution developed by Stoddard and his associate[13] would have been a much wiser choice. Not only does it seem to be the best solution developed so far, but the information presented by them was complete. After checking their statements, a particular phase of the process could have been studied which would likely have produced far more valuable results than those produced in this thesis. Unfortunately, the literature containing their findings was not encountered until too late to be of much assistance.

The results produced in the thesis work are all too few. They consist mainly of showing that an electrolytic deposit of iron can be made from the chloride bath, and that to produce a smooth, even, thick deposit, a relatively high temperature and a high current density are necessary. Review of the literature will show that each investigator made observations on conditions and bath compositions, and that each also believed his method to be the best. The latter is of course only natural, but the former causes no little trouble and confusion since it will be found that they contradict each other continually. Thus it was difficult to determine what information available was an aid or a hinderance to this study.

It was found obvious that hydrogen is the major trouble maker, for at no time was a deposit formed free of it. The last deposits obtained were the least brittle, but they were in no way as ductile as was claimed by Fischer and Langbien[8]. Getting a soft, ductile iron was, however, merely a matter of annealing for a short time in a muffle at 600°F.

Many investigators claimed that electrolytic iron is air resistant, but in this thesis work, all deposits were found to rust quickly and badly. This may have been accelerated by the large amount of the bath that was absorbed by the deposit. A number of washings were necessary each time before

it was felt that all had been eliminated. It can be seen, however, that combined solution would be conducive to rusting.

Where the deposits were even and free from cracking the bonding between iron and copper seemed excellent. Several times it was desired to reuse the same cathode for deposition under different conditions. The electrolytic iron was readily attacked by acid and quickly removed, but the thin bonding layer seemed almost acid resistant. Sanding was required to obtain the cathode free of iron.

In all but a few cases gassing at the electrode took place, and in the tests made at the higher temperatures and current densities, took place at both electrodes. Mechanical agitation was recommended by many of the previous investigators as a means of ridding the cathode of the troublesome bubbles. In the laboratory work it was found that agitation had no effect on the deposit. McMillan and Cooper state that pitting is avoided if gassing is rapid enough[10]. In the earlier tests when C.D. was high and temperature was low, the gassing was violent but pitting still occurred. In the final tests at both high C.D. and temperature the gassing was rapid and no pitting occurred. Evidently the temperature is the controlling factor.

The results of the deposition from the sulfate bath were so poor that no comparison could be made with those received in Tests No. 17 and 18.

CONCLUSIONS

A smooth, even, thick deposit can be obtained from the chloride bath. It can be formed at room temperature at a low current density, but it is better if formed at high temperature and high current density. No matter what conditions are employed, it will be brittle from the occluded hydrogen, but annealing will make it ductile. The bond between the iron and the copper will be very strong. The iron will be pure but easily rusted. Agitation has

no effect on the deposit, nor has the hydroxide of iron formed in the solution.

RECOMMENDATIONS

I would like to recommend a long range study of electrolytic iron in all of its phases. The three baths (sulfate, chloride, and sulfate-chloride) could be investigated with the idea of determining which is actually best for all around deposition. When enough information has been gathered from all three, an intensive study could then be made toward the electro-winning of iron from its ores.

There is much to be known of the chloride bath, and I would recommend further study of it to some future student. This thesis attempted to determine the conditions at which the best deposit could be obtained, and I believe that it is conclusively shown that the high temperatures and current densities are necessary. Beginning at this point, then, the student could make an examination which would eventually show how hydrogen embrittlement can be avoided.

I would recommend the solution developed by Stoddard and his associate[13] rather than the one I employed.

I would further recommend the recording of all data, no matter how trivial, so that the results obtained may be duplicated.

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